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Efficient Blue Light Emitting Diodes Using Quantum-Confined Two-Dimensional Perovskites

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Abstract

Solution-processed hybrid organic-inorganic lead halide perovskites are emerging as one of the most promising candidates for low-cost light emitting diodes (LEDs). However, due to a small exciton binding energy, it is not yet possible to achieve an efficient electroluminescence within the blue wavelength region at room temperature, as is necessary for full-spectrum light sources. Here, we demonstrate efficient blue LEDs based on the colloidal, quantum-confined 2D perovskites, with precisely controlled stacking down to one-unit-cell thickness ($n = 1$). A variety of low- k organic host compounds are used to disperse the 2D perovskites, effectively creating a matrix of the dielectric quantum wells, which significantly boosts the exciton binding energy by the dielectric confinement effect. Through the Förster resonance energy transfer, the excitons down-convert and recombine radiatively in the 2D perovskites. We report high-color-purity electroluminescence at 520 ($n = 7-10$), 492 ($n = 5$), 456 ($n = 3$), and 432 nm ($n = 1$), with record-high external quantum efficiencies of 2.31%, 0.23%, 0.024%, and 0.0040%, respectively, in the green-to-blue wavelength region.

The earth-abundant hybrid lead halide perovskites are an emerging class of direct-bandgap semiconductors for solution-processed optoelectronics^{1, 2, 3, 4}. The fact that the materials possess an optical bandgap, E_g , tunable from the visible to infrared ranges by doping with the mixed halides^{4, 5}, has further suggested promising applications in full-spectrum light sources⁶. Compared to other large-area light emitting technologies, such as the organic semiconductors⁷ and inorganic quantum dots⁸, they have shown advantages in easy synthesis, low materials cost, and high color purity⁴. These features have generated considerable research effort aimed at developing the perovskite LEDs^{9, 10, 11, 12, 13, 14, 15, 16, 17}. However, despite significant progress on the demonstration of bright electroluminescence (EL) based on the methylammonium lead halides ($\text{CH}_3\text{NH}_3\text{PbX}_3$, where X is I, Br, and Cl)^{9, 10, 11, 12, 14, 16, 17} and cesium lead halides (CsPbX_3)^{13, 15} perovskites, the reported external quantum efficiencies (EQEs) exhibit a sharp, essentially exponential decay with decreasing the emission wavelength, λ_{EL} , when moving from orange-red to green-to-blue wavelengths regions (Fig. 1a). In particular, blue EL with $\lambda_{\text{EL}} < 480$ nm has never been achieved at room temperature^{16, 17}, as is required for practical applications⁷. Our study aimed to fill this gap.

The mechanisms responsible for much lower EQE at shorter wavelengths are still not fully understood. Indeed, unlike the organic semiconductors and inorganic quantum dots, in which the Frenkel-like excitons predominate¹⁸, recent advances in perovskite photophysics have concluded that photoexcitation generates nearly 100% free carriers in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites at room temperature¹⁹. This reflects the effect of the electric-field screening by the collective orientational motion of CH_3NH_3^+ cations²⁰, which in turn results in an anomalously high dielectric constant at low frequency^{21, 22}, as well as a small exciton binding energy, E_B , of 2 - 6 meV^{20, 22, 23, 24}. Although the small E_B essentially enables a high power conversion efficiency in solar cells¹⁹, it has been considered as a significant limiting factor for efficient light emission⁴. A number of studies have further reported that the chloride-

doped bulk perovskites possess a longer exciton lifetime and diffusion length^{25, 26}, implying an even less favorable radiative recombination. Together with the observation that they generally have a lower photoluminescence quantum yield (PLQY) relative to other counterparts (e.g., ref. ¹³), one may conclude that the chloride-doped perovskites are not ideal candidates for blue LEDs⁴.

In order to promote radiative recombination, one approach is to spatially confine diffusion of carriers, thereby increasing the probability for them to meet each other. For example, by reducing the perovskite grain size down to ~ 100 nm with the nanocrystal pinning method¹⁰, the exciton diffusion length significantly reduces²⁷, such that a high EQE at $\lambda_{\text{EL}} \sim 540$ nm has been demonstrated¹⁰. However, this method does not allow a controlled chloride doping since the solubility of the chloride precursors in the regularly-used solvents (e.g., *N,N*-dimethylformamide, DMF) is low¹⁷. Moreover, an ultrathin perovskite film with complete substrate coverage has been proven technically difficult⁴. On the other hand, a more straightforward approach is to increase E_B directly by the effect of reduced dimensionality^{5, 28}, so that the perovskite materials can become more excitonic¹⁹. In addition, a large degree of blue shift can be introduced by the quantum confinement effect²⁹. However, the excitonic Bohr radius, a_B^* , in the hybrid perovskite systems is estimated to be only $\sim 1.4 - 2.0$ nm^{30, 31}. Combining with a relatively large unit cell (~ 0.6 nm), it remains challenging to reach a precise size control during synthesis. Very recently, a large degree of blue shift has been observed in the colloidal, quantum-confined two-dimensional (2D) perovskites^{31, 32, 33, 34, 35, 36, 37, 38, 39}, which can be described by $(\text{RNH}_3)_2[\text{CH}_3\text{NH}_3\text{PbX}_3]_n\text{PbX}_4$, where R is a long-chain alkyl group, and n is the stacking number of perovskite unit cells²⁹. However, to the best of our knowledge, it is not yet possible to precisely control the stacking towards predominantly one-unit-cell ($n = 1$) thickness, with a sufficiently high PLQY ($> 30\%$) at the corresponding wavelength that yields the maximum degree of blue shift, which is a prerequisite for efficient

blue LEDs. In this work, we report the first blue LEDs using the stacking-controlled, quantum-confined 2D perovskites. Colloidal 2D $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites, with precisely controlled stacking down to $n = 1$ (Fig. 1b), were synthesized and stabilized in a liquid medium, exhibiting high PLQYs (40% - 90%). By creating complexes formed between the stacking-controlled 2D perovskites and a variety of organic host compounds, for the first time, we demonstrate an important concept in harvesting radiative recombination in hybrid perovskites through the dielectric confinement effect and the Förster resonance energy transfer (FRET). For the first time, we achieve tunable EL with $\lambda_{\text{EL}} = 520, 492, 456,$ and 432 nm at room temperature, with EQEs 2.31%, 0.23%, 0.024%, and 0.0040%, respectively, which represent an enhancement by factors of $10^1 - 10^3$ compared to those reported among the perovskite LEDs in the green-to-blue wavelength region, as shown in Fig. 1a.

Perovskite Quantum Wells

A central challenge in the perovskites-based optoelectronics is how to significantly increase E_B up to a few characteristic thermal energy at room temperature ($k_B T \sim 26$ meV), in order to induce excitonic behavior. The exciton binding energy in a bulk semiconductor is given by $E_B = \mu e^4 / (2\epsilon^2 \hbar^2)$, where μ is the exciton reduced mass, e is the elementary charge, ϵ is the dielectric constant, and \hbar is the reduced Planck constant⁴⁰. Clearly, one can obtain a higher E_B by reducing the dielectric constant, which is a basic consequence of reduced dimensionality⁴⁰. Figure 1c presents the calculated in-plane and out-of-plane ϵ as a function of n in the 2D $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites using the density functional theory (DFT) (Supplementary Section S1). Note that we take into account a fractional component of the exact exchange from the Hartree-Fock (HF) theory hybridized with the DFT exchange-correlation functional at the level of the HSE06 hybrid functional. Therefore any limitation of the exchange and correlation functional utilized in the chemical description of the energy

levels can be improved. It follows that, by reducing the stacking to $n = 1$, one can gain a nearly 4 to 7 times of E_B increase relative to that in the bulk. Since E_B in the hybrid perovskites is essentially small²⁴, we infer that, with reduced dimensionality alone, the enhanced E_B may not exceed a few $k_B T$ at room temperature. This is not surprising; in fact, the classical quantum mechanical theory has predicted that in the limit of 2D semiconductor, E_B is enhanced at most up to four times compared to the bulk value^{40, 41}, which appears to be insufficient in the system considered here.

To overcome this difficulty, in view of the fact that the 2D perovskites are structurally analogous to the quantum wells (QWs)⁴², we adopt the concept of dielectric confinement⁴¹, which is realized by surrounding the 2D perovskites with wide-bandgap, low-dielectric-constant (low- k) organic semiconducting molecules, acting as barriers (Fig. 1d). Accordingly, the resulting complex consists of a matrix of the dielectric quantum wells (DQWs)⁴¹. In a DQW, the discontinuity of ϵ causes a redistribution of the electric fields of carriers, thereby reducing the effective ϵ and screening the electron-hole Coulomb coupling. Theoretically, the dielectric confinement effect enables a significant E_B boost by up to 100 times in thin wells ($< 0.5 a_B^*$)⁴¹. In addition, its long-range nature allows extension of this effect to thick wells ($> 5 a_B^*$)⁴¹, implying that even with the non-quantum-confined 2D perovskites ($n > 10$), a considerable degree of E_B enhancement is expected. A variety of fluorescent organic host compounds, which have been extensively used in the emission layer (EML) of organic light emitting diodes (OLEDs)⁴³, were chosen as the barrier materials. We demonstrate that the near-field FRET⁴⁴ occurs at the 2D perovskite/host interfaces (Fig. 1e), due to the spectral overlap between the host (donor) emission spectrum and the 2D perovskite (acceptor) absorption spectrum, allowing rapid transport of excitons through the alkyl ligands (Fig. 1d top), followed by recombination in a 2D perovskite, as will be further discussed later.

The device architecture and energy diagram for our LED device is shown in Fig. 1f

(materials and process see Supplementary Section S4). We use a typical three-layered structure, which consists of a hole-transport layer (HTL), EML, and an electron-transport layer (ETL). The EML is prepared by spin-coating a toluene solution containing the colloidal 2D perovskites and a small amount of organic host compounds. Figure 1g presents photographs of large-area ($\sim 1.5 \text{ cm}^2$) pure-green and pure-blue LEDs at room temperature, based on the 2D $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites with $n = 7\text{--}10$ and $n = 3$, respectively, demonstrating high-color-purity EL.

Stacking-Controlled Colloidal Synthesis

The 2D $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites are synthesized using modifications of the synthesis method proposed by Pérez-Prieto *et al.* (details see Supplementary Section S3)⁴⁵. In short, the perovskite precursors, lead bromide and methylammonium bromide, were dissolved in DMF, followed by dropwisely adding to a toluene solution containing two different surfactants, oleic acid and octylamine. Colloidal crystallization of perovskites was triggered immediately due to a low solubility of the precursors in toluene at room temperature. The two surfactants used here, on one hand, kinetically stabilize the polar DMF phase in the nonpolar toluene phase by reducing the interfacial tension⁴⁶, enabling slow precipitation of crystals. On the other hand, oleic acid weakly protonates octylamine to form octylammonium cations, which in turn electrostatically bind to the bromide-riched crystal surfaces. They serve as ligands to limit further growth in the out-of-plane direction, as well as to prevent restacking between individual crystals. The resulting precipitates were finally collected and re-dispersed in toluene to obtain a colloidal solution. Accordingly, the thickness of 2D perovskites is determined by the equilibrium of surfactants and precursors across two phases. Note that the above protocol fundamentally prohibits the formation of 2D perovskites with $n = 0$, due to the presence of methylammonium cations.

The amount as well as the ratio of two surfactants used in the synthesis yield colloidal dispersions with different optical properties. Through extensive experimentation, recipes were developed to obtain four high-purity ($> 90\%$) products (Supplementary Table S1), each with single emission peak. The representative absorption and photoluminescence (PL) spectra are shown in Fig. 2a. The spectra obtained from the bulk, single crystalline $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite (Supplementary Section S3) are also attached for comparison. The full width at half maximum (FWHM) for each emission spectrum is less than 25 nm, with a Stoke shift of 5 - 10 nm. The emission peaks at 517, 489, 456, and 436 nm were assigned to the 2D $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites with $n = 7-10, 5, 3$, and 1, respectively, by comparing the peak positions with those reported in solid-phase layered perovskites^{29, 47} (Supplementary Table S2). By reducing the stacking number to $n \leq 5$ ($\sim 2 a_B^*$), in addition to a blue shift in the absorption onset, a sharper and sharper excitonic absorption feature emerges, representing a clear evidence of E_B enhancement due to the quantum confinement effect. This fact is endorsed by the observation of high PLQYs (40% - 90%) in the colloidal solutions, which show an ~ 100 -fold increase compared to that in the bulk single crystal ($< 1\%$).

We examine the colloidal 2D perovskites by transmission electron microscopy (TEM), atomic force microscopy (AFM), and grazing-incidence wide-angle X-ray scattering (GIWAXS). Rectangular 2D crystals were clearly identified on TEM grids (Figs. 2b). Note that the observed dark quasi-spherical nanoparticles within the 2D structures have been suggested to be the degradation product of perovskite caused by the focused electron beam³³. Figure 2c shows TEM image of edge of a 2D perovskite stack with $n = 3$, showing an interlayer spacing of ~ 3.2 nm. On the other hand, when spin coating of the solution ($n = 3$) onto a silicon substrate, due to a relatively slow evaporation of solvent, we find the 2D perovskites thermodynamically favor to form the “face-on” orientation, or namely, the surface normal vector is perpendicular to the substrate plane. Figure 2d presents the AFM

image of micrometer-sized, isolated 2D crystals, showing a thickness of ~ 2.5 nm (also see Supplementary Fig. S1). Since the capping ligand layer is relatively soft, we suppose that there is a degree of underestimation here. To gain more insights into the thickness and orientation, the sample was subsequently analyzed by GIWAXS, as shown in Fig. 2e. The high-order diffraction peaks along $q_{xy} = -1.061 \text{ \AA}^{-1}$ are derived from a d -spacing of 0.592 nm, which is identical to the unit cell length in the bulk cubic $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite, suggesting the presence of the bulk counterpart as a minor product. The second last peak on $q_{xy} = 0$ ($q_z = 1.049 \text{ \AA}^{-1}$, or d -spacing = 0.599 nm) corresponds to the unit cell length in the 2D perovskites, with a small degree of expansion (0.007 nm) relative to that in the bulk, due to a lattice relaxation³². Other peaks along $q_{xy} = 0$, denoted as $(l \ 0 \ 0)$, where l is an integer, correspond to the self-assembled superlattice structure of 2D perovskite stacks, exhibiting high crystallinity, long-range ordering, and face-on orientation (Supplementary Table S3). The calculated interlayer spacing, which is essentially identical to the d -spacing of the $(1 \ 0 \ 0)$ superlattice peak, is therefore determined to be 3.302 nm, consistent with our TEM observation (Fig. 2c). We therefore deduce the ligand layer between two stacked 2D crystals is 0.906 nm, as shown in the molecular-dynamics simulation snapshot of our self-assembled superlattice structure with $n = 3$ (Fig. 2f, Supplementary Section S2).

Characteristics of LED Devices

Based on the stacking-controlled 2D perovskites, LED devices were fabricated (Supplementary Section S4). We demonstrate EL peaks locating at 520 (pure green, $n = 7$ -10), 492 (sky blue, $n = 5$), 456 (pure blue, $n = 3$), and 432 nm (deep blue, $n = 1$) (Fig. 3a), with only 0 - 4 nm bathochromic shifts from the corresponding PL peaks. High-color-purity emissions with FWHMs of 23, 24, 18, and 40 nm (Commission Internationale de l'Eclairage (CIE) chromaticity coordinates see Fig. S4) are exhibited. A relatively broad emission peak,

together with the presence of a shoulder peak at ~ 480 nm, were observed in our deep blue device ($n = 1$), which may be attributed to a small degree of restacking or decomposition under electrical excitation. Indeed, we notice that the stability of this particular material is not optimal, and some devices can only endure a few times of measurement.

To elucidate the effect of organic host, a series of experiments were carried out using the pure green emitter ($n = 7-10$) (Supplementary Table S4 and Fig. S6). Clearly, without using an organic host, the control device, with a simple architecture of ITO/PEDOT:PSS/Perovskite/TPBi/LiF/Al, shows a relatively modest EQE of 0.29%, which basically follows the same trend of the reported EQE - λ_{EL} values in Fig. 1a. Accordingly, we employed CBP, a widely-used organic host material in phosphorescent OLEDs⁴³, to form a complex with the 2D perovskites. At an appropriate CBP concentration, a significant enhancement in EQE (2.07 %) is achieved. In addition to the two mechanisms addressed earlier (FRET and the dielectric confinement), we attribute the efficiency enhancement to the well-separated 2D perovskites in the CBP matrix, as well as a smoother EML. Consequently, the self-quenching caused by the adjacent 2D perovskites is reduced, and the possible electrical shunts between two transport layers are minimized¹³. A slightly higher EQE of 2.31% (Fig. 3d) and a current efficiency of 8.1 cd/A were further reached by placing a thin PVK layer, which possesses a wider bandgap (Fig. 1f), after PEDOT:PSS, due to a more effective exciton confinement within EML. We also tested three other host materials (PVK, 26DCzPPy, and BCPO) but did not observe a statistically meaningful enhancement. Thereafter, the above strategies were applied to our blue light-emitting devices.

The quantum-confined 2D perovskites ($n = 1, 3$, and 5) were then tested using the developed device architecture. The current density and luminance as a function of voltage are shown Figs. 3b and 3c, respectively, followed by the calculated EQEs versus current density in Fig. 3d. For the sky-blue emitter ($n = 5$), by using CBP as the host material, we report the

highest EQE of 0.23% among all perovskite LEDs in the blue wavelength region (Fig. 1a). The device turns on at ~ 3.5 V and reaches a luminance of 8.5 cd m^{-2} at a current density of 4.7 mA/cm^2 when operated at 6.0 V. We find that the attainable luminance is not as high as that in the green device, due to the fact that the solvability of the thin 2D perovskites ($n \leq 5$) in toluene tend to be low. It reflects a low colloidal stability that may results from a low surface coverage of octylammonium ligands in these species. We believe that further optimization in ligand engineering would eventually lead to a brighter LED.

The concept proposed here further enables the pure-blue ($n = 3$) and deep-blue ($n = 1$) perovskite LEDs, which have never been achieved at room temperature. For the two emitters, we find that the emission of the CBP-doped devices does not exhibit a spectral component associated with the 2D perovskites. Instead, a broad peak centered at $\sim 380 \text{ nm}$ was observed, consistent with that in the CBP-only device (Supplementary Fig. S7). This evidence suggests an inefficient energy transfer from CBP to thin 2D perovskites. Indeed, the absorption spectra for these emitters (Fig. 2a) exhibit a sharp excitonic absorption peak, which requires a barrier material with the emission wavelength coincident with it (Supplementary Fig. S9), in order to facilitate an efficient FRET, as will be discussed later. Accordingly, BCPO, an organic host material with a lower bandgap⁴⁸, was used in our pure-blue and deep-blue devices (Supplementary Section S4). Our preliminary results demonstrate maximum EQEs of 0.024% and 0.0040%, respectively (Fig. 3d), and both devices reach a luminance of $\sim 1 \text{ cd/m}^2$ (Fig. 3c) at room temperature. Considering high PLQYs for these emitters, we believe that further device engineering will lead to a much better EQE.

Evidence for FRET from Host to 2D Perovskite

The main idea of dielectric quantum wells requires efficient energy transfer at the well-barrier interfaces to minimize non-radiative loss. Nevertheless, the insulating nature of

the interfacial ligand layer inherently introduces transport-assisted traps⁴⁹, which seriously compromise the quantum efficiency. By taking into account the relatively long ligand chain (~ 1 nm), the fluorescent host materials were chosen to harvest energy via the near-field FRET⁴⁴. Figure 4a presents the thin-film emission and absorption spectra of neat 2D perovskite ($n = 7-10$, acceptor), as well as the emission spectra of neat PVK (donor) and the donor-acceptor complex. Clearly, there is a large spectral overlap between the acceptor absorption spectrum and the donor emission spectrum, which is a prerequisite for FRET⁴⁴. Accordingly, under electrical (or photo-) excitation, the high-energy photons emitted by the donor molecules are absorbed by the acceptor species that emits low-energy photons. Other host materials considered in this work, including CBP, BCPO, and 26DCzPPy, also show spectral overlaps with our synthesized 2D perovskites to different extents (Supplementary Fig. S9). In particular, BCPO has the highest degree of spectral overlap with the pure-blue and deep-blue emitters, which in turn results in better EQEs in devices. This hypothesis is supported by the observation that, as shown in Fig. 4a, the steady-state PL of the complex exhibits a strong, dominant peak at 520 nm, consistent with the EL spectrum (Fig. 3a), while the emission for other spectral components associated with the donor (< 450 nm) is significantly quenched. Considering a decent PLQY for neat PVK, it appears that a significant amount of energy transfers from the excited energy states (mostly singlet excitons because triplet excitons are typically dark, see Fig. 1e) of donor to the conduction band (CB) of acceptor via the Förster resonance, followed by radiatively recombining with a hole in the valence band (VB).

The mechanism is confirmed by the time-resolved PL (TRPL) spectroscopy using the time-correlated single photon counting (TCSPC) setup, with the bandpass filters that allow identification of donor and acceptor emission components independently (Supplementary Section S5). Figure 4b presents the PL decays for neat donor and neat acceptor, in

comparison with those in the complex, which provides a direct evidence for the dynamics of exciton transfer. The neat acceptor decay dynamics only change slightly on surrounding the 2D perovskite with PVK, which may be attributed to a decrease of E_B . However, we observe a significant decrease in the radiative lifetime of the donor, τ_{Donor} , from 27.2 (neat donor) to 4.3 ns (donor in complex), and an increase in τ_{Donor} with increasing donor concentration (i.e., decreasing of the acceptor content, see Fig. 4b inset and Supplementary Fig. S12). These findings strongly support that FRET occurs from donor to acceptor. The decay dynamics using other host materials are also characterized (Supplementary Figs. S10 and S11), which also show similar trend and behavior.

Conclusions

Efficient blue LEDs based on the quantum-confined 2D perovskites have been demonstrated at room temperature for the first time. We have proposed two advanced concepts to harvest blue emission from $\text{CH}_3\text{NH}_3\text{PbBr}_3$ 2D perovskites: (i) precise control of stacking number *via* co-surfactant colloidal chemistry that yields a high degree of blue shift by the quantum confinement effect, and (ii) formation of perovskite dielectric quantum wells using the fluorescent, wide-bandgap, and low- k organic hosts as the barrier materials that enables efficient radiative recombination by the dielectric confinement effect and the near-field FRET. The results presented here opens an avenue towards realization of low-cost perovskite LEDs covering the entire visible spectrum. We believe that the new findings in strong coupling between organic semiconductors and hybrid perovskites will lead to a new branch of solution-processed materials for large-area optoelectronics.

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Author Contributions

C.J.S., S.K., and J.J. conceived and designed the experiments. S.K. designed, fabricated, and characterized the LED devices. J.J. synthesized and characterized the colloidal 2D perovskites. S.Y. performed the TRPL measurement. P.R. and E.J.G.S. carried out the DFT and hybrid functional simulations. M.W. and S.L. carried out the MD simulations. Y.C.C. performed the GIXD analysis. Y.C.C., G.N., and C.H. performed the TEM and AFM analysis. Y.K. performed the PESA measurement. C.J.S., S.K., J.J., and M.K. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional Information

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